

A General Approach to the Investigation of Soft Materials by Thermodynamics Formalism

G. Oylumluoglu^{*1,2}, Fevzi Büyükkılıç^{**1}, Dogan Demirhan^{***1}

¹Ege University, Faculty of Science, Department of Physics,
Izmir-TURKEY.

²Mugla University, Faculty of Arts and Sciences, Department of Physics,
Mugla-TURKEY.

Abstract

In this study, internal energy (U), electric field (E) and particle number (N) which specify the system quantities i.e. thermodynamical quantities for the proteins. In the frame of thermodynamical formalism, the relation between the heat capacity at effective field C_E and the heat capacity at total dipole moment C_M and the relations for the increment of enthalpy ΔH , entropy ΔS and Gibbs energy ΔG which come out in the dissolving of the proteins in water have been obtained. By thinking about the present system being in the heat bath the canonical distribution function, by considering the system in heat and electric field bath the macro canonical distribution function and once more by taking the system in heat and particle number bath the macro canonical distribution function have been calculated. Partition functions have been related to the macro canonical quantities with the help of the free energy. Understanding the structure of the proteins have been endeavoured by fitting the theoretical calculations to the curves of experimental results.

Keywords: thermodynamics, classical statistical mechanics, classical ensemble theory

PACS 05.70-a, 05.20-y, 05.20.Gg

* Corresponding Authors:e-mail:oylum@sci.ege.edu.tr, Phone:+90 232-3881892 (ext.2363) Fax:+90 232-3881892

** e-mail:fevzi@sci.ege.edu.tr, Phone:+90 232-3881892 (ext.2846) Fax:+90 232-3881892

*** e-mail:dogan@sci.ege.edu.tr, Phone:+90 232-3881892 (ext.2381) Fax:+90 232-3881892

1 Introduction

Now a days, a progress in the investigation of the soft materials by the methods of statistical physics is recognized. It is not possible to think a life without the soft materials; all biological structures, molecules of the genetic code, proteins and membranes contain soft materials. The soft materials form the fundamental of life as well as being an important element of future technological developments.

Statistical mechanical methods are the most practical methods in obtaining the difference between the additional heat capacities which aries in the dissolution of proteins (one of the soft materials) in water and also for the calculation of thermodynamical functions. In favour of statistical thermodynamics it is possible to explain the microscopic quantities by relating them to the macroscopic experimental results.

While thermodynamical variables of fluids are represented by the physical quantities U (energy), V (volume) and N (particle number), passing to the measurement results in the correspondence to T (temperature), P (pressure) and μ (chemical potential) consecutively [1]. In a similar manner, for the magnetic systems the thermodynamics variables are represented by the physical quantities U (energy), H (magnetic field) and N (particle number) passing to the measurement leads to a consecutive correspondence with T (temperature), M (magnetization) and μ (chemical potential) [2].

For thermodynamical quantities of the proteins; internal energy (U), electric field (E) and particle number (N) could be taken as macroscopic variables. When the system tends to thermodynamics equilibrium, to relate with thermodynamics the system is determined by internal energy parameter; temperature (T), electric field parameter; dipole moment (M) and particle number parameter; chemical potential (μ).

2 Relation between the heat capacities of proteins

By taking electric field E and total dipole moment M as thermodynamics variables the first law of thermodynamics for the proteins could be written in the form:

$$dU = TdS - MdE. \quad (1)$$

Here, the electric field is not an external field but is used to model the ice-like behavior of the water molecules around the non-polar surface. The electric field is a result of the effective behavior of the non-polar dissolvent

that is applied to protein unfolding. By taking the proteins as a soft material, thermodynamical relation between the heat capacity C_E at effective electric field and heat capacity C_M at constant total dipole moment has been put forward. Rearranging 1 one gets:

$$dQ = dU + M dE. \quad (2)$$

To constitute such a relation if firstly the internal energy U is written as the total differentials of the variable T and E one could write

$$U = U(T, E) \implies dU(T, E) = \left(\frac{\partial U}{\partial T}\right)_E dT + \left(\frac{\partial U}{\partial E}\right)_T dE \quad (3)$$

and then substituting in 1 gives

$$dQ = \left(\frac{\partial U}{\partial T}\right)_E dT + \left(\frac{\partial U}{\partial E}\right)_T dE + M dE. \quad (4)$$

Rewriting

$$dQ = \left(\frac{\partial U}{\partial T}\right)_E dT + [M + \left(\frac{\partial U}{\partial E}\right)_T] dE. \quad (5)$$

When heat capacities are defined; since $E = \text{const.}$ and $dE = 0$, 5 becomes

$$dQ = \left(\frac{\partial U}{\partial T}\right)_E dT = C_E dT. \quad (6)$$

Similarly when $M = \text{const.}$ and $dM = 0$ 5 then takes the form

$$dQ = \left(\frac{\partial U}{\partial T}\right)_E dT + [M + \left(\frac{\partial U}{\partial E}\right)_T] dE = C_M dT. \quad (7)$$

After substituting the definitions of heat capacities given by 6 and 7 into 5 one obtains

$$C_M dT = C_E dT + [M + \left(\frac{\partial U}{\partial E}\right)_T] dE. \quad (8)$$

Dividing both sides of 8 by dT for $M = \text{const.}$ and since $\frac{dE}{dT} = \left(\frac{\partial E}{\partial T}\right)_M$ one gets

$$C_M dT = C_E dT + [M + \left(\frac{\partial U}{\partial E}\right)_T] \left(\frac{\partial E}{\partial T}\right)_M. \quad (9)$$

In order to express the term in the right hand side of this equation in terms of experimentally measurable quantities, 1 could be written in the form:

$$dS = \frac{1}{T}dU + \frac{M}{T}dE. \quad (10)$$

When the total differential of the internal energy $U(T, E)$ is taken as given in 3 and substituted in 10

$$dS = \frac{1}{T}[(\frac{\partial U}{\partial T})_E dT + (\frac{\partial U}{\partial E})_T dE] + \frac{M}{T}dE \quad (11)$$

is obtained. Rearranging this equation

$$dS = \frac{1}{T}(\frac{\partial U}{\partial T})_E dT + \frac{1}{T}[(\frac{\partial U}{\partial E})_T dE + \frac{M}{T}]dE. \quad (12)$$

Similarly the total differential of the entropy $S(T, E)$ is written in the form

$$S = S(T, E) \implies dS(T, E) = (\frac{\partial S}{\partial T})_E dT + (\frac{\partial S}{\partial E})_T dE. \quad (13)$$

Since corresponding terms in 12 and 13 must be equal to each other:

$$(\frac{\partial S}{\partial T})_E = \frac{1}{T}(\frac{\partial U}{\partial T})_E \text{ and } (\frac{\partial S}{\partial E})_T = \frac{1}{T}[(\frac{\partial U}{\partial E})_T + M]. \quad (14)$$

Writing down the property of equality of the second derivatives $[\frac{\partial}{\partial E}(\frac{\partial S}{\partial T})_E = \frac{\partial}{\partial T}(\frac{\partial S}{\partial E})_T]$ is substituted, 14 becomes:

$$\frac{\partial}{\partial E}[\frac{1}{T}(\frac{\partial U}{\partial T})_E] = \frac{\partial}{\partial T}\{\frac{1}{T}[(\frac{\partial U}{\partial E})_T + M]\}. \quad (15)$$

Taking the derivatives in 15 and after simplification one obtains:

$$\frac{1}{T} \frac{\partial}{\partial E}(\frac{\partial U}{\partial T})_E = -\frac{1}{T^2}(\frac{\partial U}{\partial E})_T - \frac{M}{T^2} + \frac{1}{T} \frac{\partial}{\partial T}(\frac{\partial U}{\partial E})_T + \frac{1}{T}(\frac{\partial M}{\partial T})_E. \quad (16)$$

Since this expression is a total differential it is independent of the order of the derivative. Rewriting 16

$$\frac{\partial}{\partial E}(\frac{\partial U}{\partial T})_E = -\frac{1}{T}(\frac{\partial U}{\partial E})_T - \frac{M}{T} + \frac{\partial}{\partial T}(\frac{\partial U}{\partial E})_T + (\frac{\partial M}{\partial T})_E \quad (17)$$

and then rearranging

$$M + (\frac{\partial U}{\partial E})_T = T(\frac{\partial M}{\partial T})_E \quad (18)$$

is obtained. Now substituting 18 in 9 one finds:

$$C_M = C_E + T \left(\frac{\partial M}{\partial T} \right)_E \left(\frac{\partial E}{\partial T} \right)_M. \quad (19)$$

Using the change rule of the total differential $\left(\frac{\partial M}{\partial T} \right)_E \left(\frac{\partial T}{\partial E} \right)_M \left(\frac{\partial E}{\partial M} \right)_T = -1$ one could write $\left(\frac{\partial M}{\partial T} \right)_E = \left(\frac{\partial E}{\partial T} \right)_M \left(\frac{\partial M}{\partial E} \right)_T$. Substituting this expression in 19 gives:

$$C_M = C_E - T \left(\frac{\partial M}{\partial E} \right)_T \left[\left(\frac{\partial E}{\partial T} \right)_M \right]^2. \quad (20)$$

By taking use of Maxwell relations written for soft materials (proteins) and with the purpose of expressing in terms of the measurable parameters from thermodynamics the following definition is given

$$- \left(\frac{\partial S}{\partial M} \right)_T = \left(\frac{\partial E}{\partial T} \right)_M = \alpha_M \quad (21)$$

which transforms 19 into:

$$C_M = C_E - T \alpha_M^2 \left(\frac{\partial M}{\partial E} \right)_T. \quad (22)$$

Similarly when the definition

$$- \left(\frac{\partial M}{\partial E} \right)_T = \frac{1}{\gamma_T} \quad (23)$$

is written down 23 now takes the form:

$$C_M = C_E - T \frac{\alpha_M^2}{\gamma_T}. \quad (24)$$

3 Thermodynamics of enthalpy, entropy and gibbs energy increments

The first law of thermodynamics for the soft materials has been written by 1. When S and M are taken as direct variables, change in enthalpy reads

$$dH = TdS + EdM. \quad (25)$$

The enthalpy increment, after taking the total differentials of enthalpy $H = H(S, M)$ and entropy $S = (T, M)$, is written in the form:

$$dH = \left(\frac{\partial H}{\partial S} \right)_M dS + \left(\frac{\partial H}{\partial M} \right)_S dM \quad (26)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_M dS + \left(\frac{\partial S}{\partial M}\right)_S dM. \quad (27)$$

By substituting 26 and 27 in 25

$$dH = \left(\frac{\partial H}{\partial S}\right)_M \left(\frac{\partial S}{\partial T}\right)_M dT + \left[\left(\frac{\partial H}{\partial S}\right)_M \left(\frac{\partial S}{\partial M}\right)_T + \left(\frac{\partial H}{\partial M}\right)_S\right] dM. \quad (28)$$

is obtained. The expressions $T = \left(\frac{\partial H}{\partial S}\right)_M$, $E = \left(\frac{\partial H}{\partial M}\right)_S$ and $\frac{C_M}{T} = \left(\frac{\partial S}{\partial T}\right)_M$ are substituted in 28 and then integration of the equation leads to the enthalpy increment:

$$\Delta H = \int_{T_t}^T C_M dT + \int_{M(T_t)}^{M(T)} [E + T \left(\frac{\partial S}{\partial M}\right)_T] dM. \quad (29)$$

For the entropy increment; the total differential of entropy $S = S(T, M)$ is taken and $\left(\frac{\partial E}{\partial T}\right)_M = -\left(\frac{\partial S}{\partial M}\right)_T$ and $\frac{C_M}{T} = \left(\frac{\partial S}{\partial T}\right)_M$ are substituted, which after integration gives:

$$\Delta S = \int_{T_t}^T \frac{C_M}{T} dT + \int_{M(T_t)}^{M(T)} \left(\frac{\partial S}{\partial M}\right)_T dM. \quad (30)$$

By taking use of the first law of thermodynamics given in 1 which has been written for the soft materials and taking into consideration the parameters U, E and N of the soft materials, change in the Gibbs energy could be obtained as

$$dG = -SdT + EdM + \mu dN. \quad (31)$$

With a similar approach, the Gibbs energy increment is determined in the form

$$\Delta G = - \int_{T_t}^T SdT + \int_{M(T_t)}^{M(T)} EdM + \int_{N(T_t)}^{N(T)} \mu dN \quad (32)$$

by taking the total differentials of Gibbs energy $G = G(T, M)$ and total dipole moment $M = M(T, E)$. These expressions together with $E = \left(\frac{\partial G}{\partial M}\right)_T$ and $-S = \left(\frac{\partial G}{\partial T}\right)_M$ are substituted in 31 and then the equation is integrated.

4 Establishment of the relation between thermodynamics and statistical mechanics

Proteins is a common name of complex macromolecules which are formed by a collection of a great number of amino-acids and which play vital roles in

the life times of all of the living creatures. As a physical object, the protein molecule is a rather big polymer which is formed by thousands of atoms; in other words it is a soft matter such that from the physical point of view this is a macroscopic system.

The three dimensional structure of the proteins depends on different environmental factors inside the cell. Unfolding proteins return to their natural state when the environmental factors are removed, in manner of exhibiting the fact that the three dimensional structure of a protein solely depends on its information of the amino-acid regularity. the probable configurations of this three dimensional structure are in astronomically large order. In the thermodynamical limit ($N \rightarrow \infty$, $E \rightarrow \infty$ and $\frac{N}{E} = const.$) it is not possible to make calculations by taking into consideration each particle in the macroscopic system formed from the proteins, even by using the computer existing on Earth with highest operation capacity. Thus combination of thermodynamics and statistical physics is a necessity. In the investigation of these type of system with the help of statistical physics, the existence of a great number of systems that are identical to the system under consideration is taken into account and using the statistical methods for these system, the most probable state in which the real system could enter is the task of determination.

Statistical ensemble mean approach is one of the appealed methods in statistical mechanics. In order to constitute the statistical ensembles in the system that are interacting with its surroundings the system has to be taken into account together with its surroundings. Distribution functions are determined in the equilibrium state using the Lagrange multipliers method from statistical ensemble theory.

4.1 A general approach to the calculation of distribution function, entropy and thermodynamical potential

4.1.1 Distribution function and partition function

For a general approach to the calculations, let the parameters U , E , N of the thermodynamical system under consideration, fluctuate together. In order words, the system could exchange energy, particles as well as electric field. Probability function P which gives the distribution of the system in to microstate is a function of n , E and N . Here n is a quantum number arising from the energy dependence. Number of particles N and electric field E also depend on energy. The entropy S of the system is given by:

$$S = -k \sum_{n,E,N} P_{n,E,N} \ln P_{n,E,N}. \quad (33)$$

The following equations for the total probability, the average energy \bar{U} , average electric field \bar{E} and average number of particles \bar{N} of the system could respectively be written;

$$\sum_{n,E,N} P_{n,E,N} = 1 \quad (34)$$

$$\sum_{n,E,N} P_{n,E,N} U_{n,E,N} = \bar{U} \quad (35)$$

$$\sum_{n,E,N} P_{n,E,N} E_n = \bar{E} \quad (36)$$

$$\sum_{n,E,N} P_{n,E,N} N_n = \bar{N} \quad (37)$$

Using the maximum entropy principle, the distribution function $P_{n,E,N}$ of the system could be determined by Lagrange multipliers method. Thus the problem is; to make the entropy given by 33 maximum under the constraints given by the 34, 35, 36 and 37. In the mathematical formalism of Lagrange multipliers methods, the expression;

$$Q = -k \sum_{n,E,N} P_{n,E,N} \ln P_{n,E,N} + \alpha_1 (1 - \sum_{n,E,N} P_{n,E,N}) + \alpha_2 (\bar{U} - \sum_{n,E,N} P_{n,E,N} U_{n,E,N}) + \alpha_3 (\bar{E} - \sum_{n,E,N} P_{n,E,N} E_n) + \alpha_4 (\bar{N} - \sum_{n,E,N} P_{n,E,N} N_n) \quad (38)$$

should be maximum, where $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ are undetermined Lagrange multipliers. Differentiating Q with respect to $P_{n,E,N}$ and equating to zero one obtains:

$$P_{n,E,N} = \exp\{-(\alpha + \beta U_{n,E,N} + \theta E_n + \gamma N_n)\} \quad (39)$$

where

$$\alpha = \frac{k + \alpha_1}{k}, \beta = \frac{\alpha_2}{k}, \theta = \frac{\alpha_3}{k}, \gamma = \frac{\alpha_4}{k}. \quad (40)$$

Taking under consideration the condition in 34; 39 leads to

$$\exp\alpha = Z(\beta, \theta, \gamma) \quad (41)$$

where $Z(\beta, \theta, \gamma)$ is the partition function of the system and is given by

$$Z(\beta, \theta, \gamma) = \sum_{n,E,N} \exp -(\beta U_{n,E,N} + \theta E_n + \gamma N_n). \quad (42)$$

Making use of 41 the distribution function now becomes

$$P_{n,E,N} = \sum_{n,E,N} \frac{\exp -(\beta U_{n,E,N} + \theta E_n + \gamma N_n)}{Z(\beta, \theta, \gamma)} \quad (43)$$

where β, θ, γ are functions of the parameters U, E and N which describe the system. In the rest of the manuscript the distribution function given by 43 will be referred as macro canonical generalized distribution function.

4.1.2 Entropy

When the distribution function given by 43 is substituted in 33 and taking into account that macro quantities U, E, N peak perfectly such that they could be taken instead of their average values, the entropy of the system becomes:

$$S = k\beta U + k\theta E + k\gamma N + k \ln Z(\beta, \theta, \gamma) \quad (44)$$

4.1.3 Determination of the Lagrange multipliers

With the purpose of obtaining the physical counterparts of the multipliers β, θ and γ , the definition of temperature T , total dipole moment M and chemical potential μ are made;

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{E,N} \quad (45)$$

$$M = T \left(\frac{\partial S}{\partial E} \right)_{U,N} \quad (46)$$

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,E}. \quad (47)$$

Furthermore, after differentiation it is easy to show that;

$$\frac{1}{Z} \left(\frac{\partial Z}{\partial \beta} \right)_{\theta, \gamma} = -\overline{U} = -U \quad (48)$$

$$\frac{1}{Z} \left(\frac{\partial Z}{\partial \theta} \right)_{\beta, \gamma} = -\overline{E} = -E \quad (49)$$

$$\frac{1}{Z} \left(\frac{\partial Z}{\partial \gamma} \right)_{\beta, \gamma} = -\overline{N} = -N. \quad (50)$$

In the above equations, instead of the average values U , E and N are taken.

Substituting 44 in 45 and making use of 48 one ends up with:

$$\beta = \frac{1}{kT}. \quad (51)$$

Similarly substituting of 44 in 46 and 47 respectively leads to:

$$\theta = \frac{M}{kT} \quad (52)$$

$$\gamma = -\frac{\mu}{kT}. \quad (53)$$

In the content of these calculations, distribution function 43 takes form:

$$P_{n,E,N} = \frac{\exp - \beta(U_{n,E,N} + ME_n - \mu N_n)}{Z(T, M, \mu)} \quad (54)$$

and for the partition function one obtains:

$$Z_{n,E,N} = \sum_{n,E,N} \exp - \beta(U_{n,E,N} + ME_n - \mu N_n). \quad (55)$$

On the other hand for the entropy given by 44

$$S = \frac{U}{T} + \frac{ME}{T} - \frac{\mu N}{T} + k \ln Z \quad (56)$$

could be written.

4.1.4 Thermodynamical potential

Commencing with the entropy namely 56 and considering

$$\Phi(T, M, \mu) = -kT \ln Z \quad (57)$$

as thermodynamical potential one ends up with

$$\Phi(T, M, \mu) = F + ME - \mu N \quad (58)$$

where $F = U - TS$ is the Helmholtz free energy. 58 could also be written in a different form:

$$\Phi(T, M, \mu) = G - \mu N \quad (59)$$

where $G = U - TS + ME$ is the Gibbs free energy.

4.2 Obtaining the canonical distributions from the generalized distribution

The micro canonical, canonical and macro canonical distributions that are frequently met in the literature [3] can be obtained as the special cases of the generalized distribution, which is given by 43.

4.2.1 System in a heat bath: canonical distribution

Thermodynamical systems which obey micro canonical distributions are systems isolated from energy, electric field and particle number exchanges. Therefore, energy has a unique value.

In the thermodynamical systems governed by the canonical distribution there is energy exchange but the system is isolated from electric field and particle number exchanges. For this system $\alpha_1 \neq 0$, $\alpha_2 \neq 0$, $\alpha_3 = 0$, and $\alpha_4 = 0$. When the corresponding multipliers are substituted in 43 the distribution function takes the form;

$$P_n = \frac{1}{Z} \exp(-\beta U_n) \quad (60)$$

and the partition function 42 becomes

$$Z = \sum_n \exp - \beta U_n. \quad (61)$$

One order hand the entropy expression given by 44 reduces to

$$S = \frac{U}{T} + k \ln Z. \quad (62)$$

Meanwhile the thermodynamical potential of the system could be written as

$$F = U - TS \quad (63)$$

where $F = -kT \ln Z$ is Helmholtz free energy.

Statistical mechanics plays the role of bridging the understanding of the physical quantities in terms of their microscopic counterparts. The energy of the proteins system is determined by:

$$U = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z. \quad (64)$$

The heat capacity at effective electric field has been calculated from the expressions of partition function and internal energy giving;

$$C_E = -k\beta^2 \left(\frac{\partial U}{\partial \beta} \right)_E. \quad (65)$$

Heat capacity at constant total dipole moment is obtained by making use of expression [4]

$$C_M = C_E - T \left(\frac{\partial M}{\partial E} \right)_T \left[\left(\frac{\partial E}{\partial T} \right)_M \right]^2. \quad (66)$$

In a canonical ensemble, connection with thermodynamics is not established by entropy but with Helmholtz free energy. The following relations are written between Helmholtz free energy and the thermodynamical quantities;

Entropy;

$$S = -\left(\frac{\partial F}{\partial T} \right)_E \quad (67)$$

Total dipole moment;

$$M = -\left(\frac{\partial F}{\partial E} \right)_T. \quad (68)$$

4.2.2 System in a heat and electric field bath: macro canonical distribution

Let us take into account the system where energy U and electric field E fluctuate but the number of particles is constant. For this case $\alpha_1 \neq 0$, $\alpha_2 \neq 0$, $\alpha_3 \neq 0$, and $\alpha_4 = 0$. In a similar manner to the above mentioned distributions, the distribution function

$$P_{n,E} = \frac{1}{\Xi} \exp -\beta(U_{n,N} - ME_n) \quad (69)$$

the partition function

$$\Xi = \sum_{n,E} \exp -\beta(U_{n,N} - ME_n) \quad (70)$$

the entropy

$$S = \frac{U}{T} + \frac{ME}{T} + k \ln \Xi \quad (71)$$

and thermodynamical potential

$$\Phi = F + ME \quad (72)$$

are obtained, where $\Phi = -kT \ln \Xi$.

4.2.3 System in a heat and particle bath: macro canonical distribution

In thermodynamical systems obeying the macro canonical distribution, the system is in a heat bath and material bath. For such a system $\alpha_1 \neq 0$, $\alpha_2 \neq 0$, $\alpha_3 = 0$, and $\alpha_4 \neq 0$. When the corresponding multipliers are determined and substituting in 43, distribution function takes the form:

$$P_{n,N} = \frac{1}{\Xi} \exp - \beta(U_{n,N} - \mu N_n). \quad (73)$$

For the systems obeying macro canonical distribution, 42, which gives the partition function, reads

$$\Xi = \sum_{n,N} \exp - \beta(U_{n,N} - \mu N_n) \quad (74)$$

the entropy equation now becomes

$$S = \frac{U}{T} - \frac{\mu N}{T} + k \ln \Xi \quad (75)$$

and thermodynamical potential of the system is

$$\Phi = F - \mu N. \quad (76)$$

In the macro canonical ensemble, in the first approximation, when the equation expressing the canonical ensemble is extended to macro canonical case without putting any restriction on the particle number the, following equation could be used [5];

$$\Phi(T, E, \mu) = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\exp \left(\frac{\mu}{kT} \right) Z(T, E, N=1) \right]^N. \quad (77)$$

As it is recognized, the partition function is summed over by weighing with Gibbs factor which has been used in the calculation of undistinguishable particles. When the sum in 77 is calculated;

$$\Phi(T, E, z) = \exp z Z(T, E, N = 1) \quad (78)$$

is obtained. In this equation, μ being the chemical potential, the term $z = \exp(\beta\mu)$ corresponds to the pH of the system and it is a weighing factor. The energy of the system is given by

$$U = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\mu, E} \quad (79)$$

and it is determined by differentiation after substitution of the partition function. In terms of this grand potential, the expressions for the other thermodynamical quantities are given by;

Entropy;

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\mu, E} \quad (80)$$

Total dipole moment;

$$M = -\left(\frac{\partial \Phi}{\partial E}\right)_{\mu, T} \quad (81)$$

Particle number;

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T, E} \quad (82)$$

Enthalpy, Gibbs energy and entropy increments and physical quantities ϵ , b and μ in 65, 66, 67 and 68 that has been obtained in this semi phenomenological theory are determined by fitting experimental results given by [6, 7].

5 Conclusions

In this study, for the soft matters in the frame of thermodynamics formalism, the relation between the heat capacities in 24, ΔH enthalpy, ΔS entropy and Gibbs energy ΔG increments have been calculated and presented in 29, 30 and 32 respectively. Establishment of the relation between the thermodynamics and statistical mechanics ha been done with the help of the partition function and given by 56, 62, 70 and 75. Calculation of the partition functions for proteins (soft materials) with multi molecules exhibits difficulties. Therefore the partition function of a single molecules is obtained with the mean field approximation and then multiplied by N. The partition function is related to the parameters ϵ , b and μ which determined the properties of the molecule. In 24 presented here; C_M is taken from experimental data, C_E

is theoretically calculated and the above mentioned parameters are obtained by fitting to the experimental results.

On the other hand in the calculation of the increments of enthalpy ΔH , entropy ΔS and Gibbs energy ΔG , one proceeds in a similar manner. As an example, in the calculation of the entropy increments, as mentioned above C_M is taken from the experimental data and the term related with entropy is obtained from 67. As a conclusion one could say that; the structure of the proteins (soft materials) might be understood by the thermodynamics, statistical mechanics and experimental studies triplet using this semi phenomenological approach.

The significance of the electric field is to model the ice-like behavior exhibited by the water molecules around the non-polar surfaces which is a kind of stiffness [8]. Here this is not a real external electric field but the effective behavior of the non-polar dissolute enforced upon in the protein unfolding. It could also be possible to approach to this problem by considering the protein as a rigid body. However, in the proteins which are example of the soft matters, the benefit of determination of the expression which displays the thermodynamical relation between the heat capacity at effective electric field C_E and the heat capacity at constant total dipole moment C_M is evident.

As it could be seen from 24 which shows the thermodynamical relation between the heat capacity at effective electric field C_E and the heat capacity at constant total dipole moment C_M , the difference between the heat capacities depends linearly on temperature. However results of experimental studies indicate a nonlinear dependence. This in turn implies the necessity of taking into account the internal structure of proteins. C_E given in 24 could easily be calculated theoretically and if C_M expression is obtained experimentally then this enables the system to be investigated in terms of thermodynamical quantities.

References

- [1] Stanley, H.E.: Introduction to phase transitions and critical phenomena, Oxford University Press (1971)
- [2] Anderson, J.C.: Magnetism and magnetic materials, *Modern Electrical Studies*, John Wiley (1965)
- [3] Turner, R.E., Betts, M.A.: Introductory statistical mechanics, University Printing House, Cambridge (1974)

- [4] Reif, F.: Fundamentals of statistical and thermal physics, McGraw Hill Book Company, New York (1965)
- [5] Griner, W., Neise, L., Stcker, H.: Thermodynamics and statistical mechanics, Springer-Verlag (1995)
- [6] Privalov, P.L.: Thermodyanmics of protein folding, *J. Chem. Thermodynamics* **29**, 447–474 (1997)
- [7] Creighton, T.E.: Protein folding, W.H. Freeman and Company, New York (2000)
- [8] Bakk, A., Hoye, J.S., Hansen, H.: Specific heat upon aqueous unfolding of the protein interior: atheoretical approch, *Physica A* **304**, 355–361 (2001)